



The 27th Professor J.N. Mukherjee-ISSS Foundation Lecture*

Organic Nitrogen Mineralization in Submerged Soils: The Role of Inorganic Electron Acceptors

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I am most thankful to the Indian Society of Soil Science (ISSS) for inviting and giving me the privilege to deliver the prestigious 27th Professor J.N. Mukherjee—ISSS Foundation Lecture at the 74th Annual Convention of the Society during 22-25 December in Delhi. The ISSS Secretary Dr. R.K. Rattan very kindly gave me the choice of a topic related to basic aspects of Soil Science.

Professor Mukherjee was outstanding teacher, researcher and equally importantly, the founder Secretary of the ISSS. I take this opportunity to pay my humble homage to Professor Mukherjee. For this lecture, I have chosen the topic “Organic nitrogen mineralization in submerged soils: the role of inorganic electron acceptors”. The topic is of much significance and importance as the organic mineralization in lowland soils regulates wetland rice productivity and sustainability and environmental quality. The importance of lowland rice ecosystem to global rice supply cannot be overemphasized.

Why Nitrogen Mineralization?

The mineralization or ammonification (ammonium production) of organic nitrogen (N) is a key process that regulates the bioavailability of N, wetland productivity and environmental quality (Reddy and De Laune 2008). Thus N mineralization in lowland ecosystem assumes much importance for both agricultural productivity and ecological health.

Nitrogen mineralization in soils is the biological transformation of organic forms of N to ammonium and this process can occur in either aerobic or anaerobic conditions. However, the N mineralization process in submerged soils stops at ammonium pro-

duction because of lack of oxygen. Ammonium in flooded soils and sediments is produced by reductive deamination (the conversion of amino acid-N to ammonia via saturated acids) of amino acids and degradation of purines, with the release of ammonia, carbon dioxide and volatile fatty acids as the end products (Ponnamperuma 1972; Kyuma 2004). Ammonium is the most reduced form of inorganic N with an oxidation state of -3 . Ammonium is stable under reduced conditions of lowland soils and thus accumulates in flooded soils (Ponnamperuma 1972; Ando *et al.* 1992; Narteh and Sahrawat 1999, 2000; White and Reddy 2001; Sahrawat and Narteh 2001).

Moreover, because of lack of oxygen the ammonification of organic N is slower under anaerobic condition due to less efficient and incomplete decomposition of organic N (White and Reddy; Sahrawat 2004a). This is caused by the lack of oxygen, which is the most efficient electron acceptor. In the absence of molecular oxygen, the decomposition of organic matter and the release of ammonium are supported by electron acceptors, which are less efficient. The objective of this paper is to critically assess the role of inorganic electron acceptors in the mineralization of organic N in submerged soils. Assessing the N-supplying capacity of lowland soils is a prerequisite for an efficient use of fertilizer N (Sahrawat 1983; Narteh and Sahrawat 1998).

General Factors Affecting N Mineralization

The mineralization of organic N in lowland soils and sediments is influenced by soil, environmental and agronomic factors. The most important among these are temperature, soil water regime, microbial activity and microbial biomass, pH, redox potential, C:N ratio, the loadings of alternate acceptors, amount and nature of soil clay, cation exchange capacity of

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soil, nature and amounts of salts, inputs and quality of organic materials, amount and quality of soil organic matter and the supply of other nutrients such as phosphorus among others involved in the decomposition of organic matter and release of ammonium (Savant and McClellan 1987; Lindau *et al.* 1989; Sahrawat 1983, 1998; Ireneo *et al.* 1996; White and Reddy 2001; Li *et al.* 2003; Sano *et al.* 2006; Inamura *et al.* 2009; Sahrawat 2010).

In a recent review of global literature on the factors influencing the mineralization of organic N in submerged soils and sediments, Sahrawat (2010) concluded that the main environmental factors that regulate the decomposition of soil organic matter and release of ammonium-N, which also govern the primary productivity of lowlands, include water regime, temperature, organic matter quantity and quality and the loadings of inorganic electron acceptors.

Moreover, the redox status of a lowland soil system impacts organic N mineralization (White and Reddy 2001); and the redox potential in the flooded system is controlled by the quantity and quality of organic matter and the loading of inorganic electron acceptors (Achnich *et al.* 1995; Narteh and Sahrawat 1999, 2000; White and Reddy 2001; Sahrawat 2004a, b, c; Alewell *et al.* 2008). A range of redox potentials are encountered in lowland soils and sediments (Table 1).

The availability and amount of inorganic electron acceptors including oxygen, nitrate, manganic-manganese, ferric-iron, sulfate and carbon dioxide regulate redox potential. The reduction process in a submerged soil system follows the sequence—oxygen, nitrate, manganese, iron, sulfate and carbon dioxide (Table 2).

Inorganic Electron Acceptors and N Mineralization

The principal redox couples in sequence in typical submerged soils are: O_2/H_2O , NO_3^-/N_2 , Mn (IV, III)/Mn (II), Fe (III)/Fe (II), SO_4^{2-}/H_2S and CO_2/CH_4 . The main alternate inorganic electron acceptors in submerged soils include dissolved O_2 , NO_3^- , Fe (III),

Table 1. The range of redox potentials (Eh) encountered in well-drained and submerged soils and sediments (adapted from Patrick and Reddy 1978)

Soil water condition	Redox potential (mV)
Well-drained (Aerated)	+ 700 to + 800
Moderately reduced	+ 400 to + 200
Reduced	+ 100 to - 100
Highly reduced	- 100 to - 300

Table 2. Approximate redox potentials at which the main oxidized components in submerged soils and sediments become unstable (adapted from Patrick and Reddy 1978)

Reaction	Redox potential (mV)
$O_2 - H_2O$	+ 380 to + 320
$NO_3^- - N_2, Mn^{4+} - Mn^{2+}$	+ 280 to + 220
$Fe^{3+} - Fe^{2+}$	+ 180 to + 150
$SO_4^{2-} - S^{2-}$	- 120 to - 180
$CO_2 - CH_4$	- 200 to - 280

SO_4^{2-} and CO_2 (Sahrawat 2004c). The final products of reduction in submerged soils are Fe (II), H_2S and CH_4 , although intermediate products such as dissolved H_2 and H_2S are also found in submerged soils and sediments (Gao *et al.* 2002).

When the soil is submerged into water, oxygen in the system is rapidly consumed during aerobic microbial respiration. This is followed by successive use of NO_3^- , Mn (IV), Fe (III) and SO_4^{2-} as electron acceptors in anaerobic microbial respiration (Patrick and Reddy 1978; Ponnampereuma 1984). In the absence of oxygen, facultative and obligate anaerobes use the dissimilation products of carbohydrates and proteins as electron acceptors in their respiration (Ponnampereuma 1984). In tropical rice soils, Fe is the main electron acceptor. Iron occurs as Fe (III) oxides and oxyhydroxides, and in the structure of clay minerals (Stucki 1988).

Soil reduction in submerged soils and sediments is measured by redox potential (Eh) and expressed in mV; and the measured Eh can be explained by the concentration of selected redox systems. Dissolved O_2 , NO_3^- and SO_4^{2-} are relatively electrode-insensitive and others, especially Fe (III) play important role in the soil reduction, measured by Eh (Berner 1981; Gao *et al.* 2002; Bartlett 1999; Fiedler *et al.* 2007). The results of a field experiment showed that the measured Eh showed a higher correlation to redox species Mn (II) ($r^2 = 0.76$), Fe (II) ($r^2 = 0.73$) and methane ($r^2 = 0.76$) than to dissolved oxygen, nitrate and sulfate-S (Gao *et al.* 2002). The range of Eh generally encountered in submerged soils and sediments (Table 1) and the approximate Eh values at which the main oxidized components in submerged soils become unstable (Table 2) serve as a guideline for both classifying soil reduction as well as the availability of dominant inorganic electron acceptors under diverse soil moisture regime (Patrick and Reddy 1978; Sahrawat 2004c).

Narteh and Sahrawat (1999) showed that at 4 weeks after flooding of West African soils, the soil

solution Eh can be predicted from the concentration of Fe (II) in soil solution and soil solution pH:

$$Eh = 409 - 4.09 \log Fe(II) - 59 pH; R^2 = 0.99 \quad \dots(1)$$

Furthermore, the changes in soil solution pH corresponded to changes in soil solution Eh. The stability in Eh – pH relationship was recorded at the 4 week after flooding and the relationship was described by the following equation (Narteh and Sahrawat 1999):

$$\Delta Eh = -16 - 48 \Delta pH; R^2 = 0.84 \quad \dots(2)$$

Geological evidences suggest that alternate electron acceptors such as Fe (III) reduction has been an important process for organic matter oxidation since early in the Earth's biotic history. The strong correlation in the occurrence of isotopically light carbonates and magnetite in the pre-Cambrian banded Fe formations indicates that organic matter oxidation and ammonium release was coupled to Fe (III) reduction in this environment (for review see Lovely 1995; Reddy and De Laune 2008). In addition to Fe redox, the C metabolism in wetland sediments is also affected by other terminal electron-accepting reactions involving oxygen, nitrate, manganese and sulfate reduction (Wesrtrich and Berner 1984; Lovley and Phillips 1986; Canfield *et al.* 1993).

The chemistry especially of tropical submerged soils and sediments is dominated by Fe redox systems and the number of studies reporting the role of Fe as an alternate electron acceptor in organic matter oxidation and ammonium production in submerged soils and sediments has been larger than with other inorganic electron acceptors (Lovely 1995; Reddy and De Laune 2008; Sahrawat 2010).

In a study of 15 West African rice soils, Sahrawat and Narteh (2002, 2003) showed that the concentration of ammonium-N, other macro- and micro-nutrients released under submerged conditions in these soils, measured by EC of the soil solution, was significantly correlated to organic C and reducible Fe extracted by EDTA. These results show the importance of reducible Fe on the release of ammonium-N and other nutrients in soil solution of submerged rice soils that are rich in Fe. Moreover, ammonium sorption/fixation and release dynamics in submerged tropical rice soils is greatly influenced by Fe redox reactions (Sahrawat 2004b). During flooding, the ammonium sorbed under non-submerged conditions by amorphous Fe, is released following the reduction of Fe (III) to Fe (II). Under reduced conditions in soils and sediments, the sorbed ammonium is released by both Fe (III) reduction to Fe (II) and exchange with Fe (II) (Davison 1993; Sahrawat 2004b).

The mineralization of organic N in diverse West African rice soils showed that although extractable Fe was not directly correlated to ammonium produced under waterlogged condition, its inclusion in the multiple regression analysis improved the prediction of ammonium production (Narteh and Sahrawat 1997). The results of further studies demonstrated that the ammonium-N produced under flooded condition in 15 tropical soils was significantly correlated to organic C ($r = 0.79$, $n = 15$) and Fe extracted by EDTA ($r = 0.86$) or ammonium oxalate ($r = 0.75$). Multiple regression analysis of the results showed that ammonium production in soils or ammonium released in soil solution can be predicted from organic C and EDTA or ammonium oxalate extractable Fe (Narteh and Sahrawat 2000; Sahrawat and Narteh 2001, 2003).

It is suggested that EDTA and ammonium oxalate solutions extract fractions of amorphous Fe that are easily reducible and are used as the measure of the activity of poorly crystalline Fe (III) oxides in soils (Schwertmann 1966; Borggaard 1979; Wahid and Kamalam 1993). Moreover, the amorphous Fe fractions contribute to Fe (II) production in reduced (Eh 150-180 mV) soils and sediments. The intensity of Fe (II) production increases with a decrease in the crystallinity of the pedogenic Fe (III) oxides and hydroxides and with an increase in the easily mineralizable organic substances (Schwertmann 1966; Patrick *et al.* 1973; Munch and Ottow 1980; Wahid and Kamalam 1993; Olaleye *et al.* 2000; Fiedler *et al.* 2007).

From studies made with West African rice soils, Sahrawat and Narteh (2003) concluded that a chemical index based on organic matter and reducible Fe contents can be used for an improved prediction of ammonium production in submerged soils. From their work, multiple regression equations relating organic C and reducible Fe [extracted by EDTA (EDTA-Fe) or ammonium oxalate (ammonium oxalate-Fe)] to ammonium N released were developed, which can be used for determining the N mineralization potential of wetland soils. The relationships of organic C and reducible Fe with N mineralization or ammonium produced in 15 West African soils were represented by the following regression equations:

$$\text{Mineralizable N (mg kg soil}^{-1}\text{)} = 16.4 + 1.320 \text{ Organic C (g kg}^{-1}\text{)} + 0.0369 \text{ EDTA-Fe (mg kg}^{-1}\text{)}; R^2 = 0.85 \quad \dots(3)$$

$$\text{Mineralizable N (mg kg}^{-1}\text{ soil)} = 11.14 + 1.805 \text{ Organic C (g kg}^{-1}\text{)} + 0.00469 \text{ Ammonium oxalate-Fe (mg kg}^{-1}\text{)}; R^2 = 0.81 \quad \dots(4)$$

Table 3. Distribution of 15 West African rice soils according to mineralizable N (Min-N) released under anaerobic incubation and associated organic C and EDTA (EDTA-Fe) or ammonium oxalate extractable Fe (Amox-Fe) contents (adapted from Sahrawat and Narteh 2003)

Min-N (mg kg ⁻¹ soil)	No. of soils (g kg ⁻¹ soil)	Organic C (mg kg ⁻¹ soil)	EDTA-Fe	Amox-Fe
86 - 166	4	23.0 - 46.0	150 - 2200	1875 - 11412
55 - 77	5	9.2 - 23.2	325 - 800	1100 - 6750
21 - 50	6	7.4 - 15.6	125 - 600	925 - 3562

The results showed that soils high in both organic C and reducible Fe were high in mineralizable N, while soils low in organic C or reducible Fe had relatively lower contents of mineralizable N (Table 3). These results reinforce highly significant correlations between mineralizable N and organic C and reducible Fe extracted by EDTA or ammonium oxalate (Sahrawat and Narteh 2001).

Redox potential of flooded soils and sediment impacts organic N mineralization (Lindau *et al.* 1989; White and Reddy 2001), which in turn is regulated by soil organic matter quantity and quality and the loadings of alternate electron acceptors. For example, White and Reddy (2001) studied the effects of aerobic (presence of O₂), NO₃⁻ reducing, SO₄²⁻ reducing and methanogenic experimental conditions on potential organic N mineralization. Soil samples from 0-10 and 10-30 cm depths were collected from eight sites along a 10-km eutrophic gradient in the northern Everglades, Florida (USA). The results showed that the organic N mineralization rates decreased from aerobic conditions to NO₃⁻ and SO₄²⁻ reducing conditions to methanogenic conditions. The N mineralized in surface (0-15 cm) of lowland soils after 15 days of incubation followed the order: aerobic condition (ammonium-N released was 143 mg kg⁻¹ soil) > nitrate reducing redox potential condition (17 mg kg⁻¹ soil) > sulfate reducing redox potential (9 mg kg⁻¹ soil) > methanogenic redox potential (5 mg kg⁻¹ soil). These results demonstrated that organic N mineralization in submerged soils is influenced by soil reduction measured by redox potential; and the amount of N mineralized was largest under aerobic condition and it was lowest under highly reduced condition or methanogenic condition (White and Reddy 2001).

Perspectives

Decomposition of organic matter and the release of ammonium in wetland ecosystem is fundamentally different than under aerobic upland systems. While in aerobic soils organic matter is efficiently and completely oxidized using O₂ as a terminal electron acceptor, the anaerobic decomposition of or-

ganic matter in submerged soils is inefficient, incomplete and slower (Sahrawat 2004a; Reddy and De Laune 2008; Keller *et al.* 2009).

The redox systems, controlled by alternate electron acceptors regulate ammonium production in submerged soils and sediments. However, since Fe is present in high amounts especially in tropical soils, it exerts a dominant role not only in soil reduction but also in the release of ammonium in submerged rice soils. In the absence of oxygen, alternate inorganic electron acceptors support organic matter oxidation and ammonium production (Sahrawat and Narteh 2003; Reddy and De Laune 2008), although the mechanisms involved, especially in ammonium production are not fully understood.

A better understanding of the role of alternate inorganic electron acceptors such as reducible Fe in N mineralization in submerged soils and sediments will lead to the development of improved methods for assessing and predicting soil N mineralization and its bioavailability. There is an obvious need to conduct further research in understanding the role of redox reactions involving inorganic electron acceptors in influencing N supply and cycling, controlling wetland productivity, regulating environmental quality and determining the sustainability of the wetland ecosystems. Obviously, the research in this area is of scientific, environmental and agricultural interest.

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About the Lecture

This Lecture is being organized by the Indian Society of Soil Science to commemorate its foundation in 1934 and its founder - Professor J.N. Mukherjee, a doyen of Colloid and Soil Sciences, known internationally. The lecture was first instituted in 1983 as a part of felicitations to Professor J.N. Mukherjee on the eve of his 90th birthday celebration (on April 23, 1983). Unfortunately, after a few days, on May 10, 1983, the members of the Society had to mourn his demise. A short life sketch of this reputed scientist and his achievements can be seen in an earlier issue of this Journal (*J. Indian Soc. Soil Sci.* Vol. **31**, pp 350-358, year 1983), while a brief account of the birth, growth and achievements of the Society is available in another publication of the Society (*Souvenir*, pp 26-35), which was released during the Diamond Jubilee Celebration of the Society on 28th November, 1994.

Most appropriately, the privilege and honour of delivering the First Lecture in this series went to another internationally known Soil Scientist, Dr. S.P. Raychaudhuri - one of the brilliant students of Professor Mukherjee (*J. Indian Soc. Soil Sci.* Vol. **31**, pp 359-363, year 1983). The subsequent lectures in this series were delivered by Prof. L.N. Mandal (1984), Dr. G.S. Sekhon (1985), Dr. K.V. Raman (1986), Dr. N. Panda (1987), Dr. S. Patnaik (1988), Dr. N.T. Singh (1989), Dr. I.P. Abrol (1990), Dr. S.B. Varade (1991), Dr. Raj Pal (1992), Dr. S.S. Khanna (1993), Dr. U.S. Sreeramulu (1994) Dr. N.N. Goswami (1995), Dr. P.N. Takkar (1996), Dr. S.K. Ghosh (1997), Dr. S.R. Poonia (1998), Dr. D.K. Das (1999), Dr. N.K. Tomar (2000), Dr. S.K. Sanyal (2001), Dr. N.S. Pasricha (2002), Dr. D.K. Pal (2003), Dr. Sridhar Komarneni (2004), Dr. A.K. Sarkar (2005), Dr. Bijay Singh (2006), Dr. Kunal Ghosh (2007) and Dr. K.N. Tiwari (2008).

Twenty-seventh lecture in 2009 was delivered by Dr. Kanwar L. Sahrawat in Delhi and his biography in brief appears in the next section. This is for the information of the Readers that all the Prof. J.N. Mukherjee-ISSS Foundation lectures delivered up to year 2002 have been published as the ISSS Bulletin No. 21.

About the Speaker

Dr. Kanwar L. Sahrawat received M.Sc. (1969) and Ph.D. (1973) degrees in Soil Science and Agricultural Chemistry from the Indian Agricultural Research Institute (IARI), New Delhi. Dr. Sahrawat was awarded Seth Lachhi Ram Chudiwala medal in 1974 by IARI for his Ph.D. thesis research on the development of nitrification inhibitors from indigenous resources, as an outstanding contribution in the area of agricultural chemicals.

Dr. Sahrawat started his scientific career as a research associate (1973-1975) in ICRISAT, Patancheru, India. He successively worked as a post-doctoral research fellow (1975-1978) with Dr. F. N. Ponnampuruma in IRRI, Philippines, Soil Chemist/Senior Soil Chemist (1978-1991) in ICRISAT, India and principal soil chemist (1991-2001) at the West Africa Rice Development Association (now Africa Rice Center) (WARDA). Dr. Sahrawat spent his entire professional career working in the CGIAR system. In WARDA, he was also Coordinator of the project on "Integrated management of iron toxicity in lowland rice" and the Task Force on "Problem soils". During his stint with ICRISAT (India) and WARDA (Bouake, Ivory Coast), Dr. Sahrawat had an opportunity to establish soil chemistry laboratories. During 1983-1984, Dr. Sahrawat was on a sabbatical leave, from ICRISAT, at the Soil Science Department, University of Wisconsin-Madison, USA and worked with Professor D. R. Keeney. Since May 2002, Dr. Sahrawat has been working as a consultant/visiting

scientist at ICRISAT-India; and his research pertains to the diagnosis and management of nutrient problems in the watersheds in India, for enhancing productivity and quality of rainfed cropping systems.

Dr. Sahrawat has published over 300 technical papers including 200 papers in refereed international and national journals, bulletins, edited conference proceedings and chapters in *Advances in Agronomy*, *Advances in Soil Science*, *Encyclopedia of Soil Science*, *Soil Science Society of America Special Publication no. 58* and other books. He has extensively conducted research on the chemistry of nitrogen, phosphorus and iron, both deficiency and toxicity. He led research on the chemistry of wetland soils and the management of acid soil related infertility in uplands in West Africa. This research has been very rewarding scientifically and for practical management of "opportunity soils". Dr. Sahrawat always applied basic Chemistry principles for developing or improving existing methods of soil and plant analysis for diagnostic and routine analyses purposes. This effort has resulted in the development of techniques for rapid and precise analysis of soil and plant materials.

Dr. Sahrawat has served as an Affiliate Faculty of the post-graduate school, APAU (now ANGRAU) (1978-1991, 2007-), Rajendra Nagar and University of Ghana (1993-2001), Accra, Ghana and supervised the thesis research of M.Sc. and Ph.D. students in the general area of Soil Chemistry, Biochemistry, Fertility and Plant Nutrition. Dr. Sahrawat served as a member of the International Council on Plant Nutrition (1978-1993) and Adviser (1998-2004), International Foundation for Science, Stockholm, Sweden. He is a recipient of the fellowship (1999) of the National Academy of Agricultural Sciences, India. Dr. Sahrawat received a certificate of appreciation from WARDA in 2001 for his outstanding contribution to rice research and development through service as a Principal Soil Scientist.